

026 Rec'd PCT/PTO 25 JAN 2001

SUBSTITUTE FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER
12683-003001**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**U.S. APPLICATION NO. (If Known, see 37 CFR 1.5)
09/744531INTERNATIONAL APPLICATION NO.
PCT/IB99/01326INTERNATIONAL FILING DATE
27 July 1999PRIORITY DATE CLAIMED
29 July 1998

TITLE OF INVENTION

BENEFICATION OF TITANIA SLAG BY OXIDATION AND REDUCTION TREATMENT

APPLICANT(S) FOR DO/EO/US Jacobus Philippus Van Dyk, Nanne Mattheus Vegter, Cornelia Petronella Visser, Thomas De Lange, John David Winter, Ernest Alan Walpone and Johannes Nell

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☐ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (unsigned)
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 16 below concern other documents or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

☐
☐
☐
☐
☐
CERTIFICATE OF MAILING BY EXPRESS MAIL

Express Mail Label No.

12683-003001

I hereby certify under 37 CFR §1.10 that this correspondence is being deposited with the United States Postal Service as Express Mail Post Office to Addressee with sufficient postage on the date indicated below and is addressed to the Commissioner for Patents, Washington, D.C. 20231.

Date of Deposit

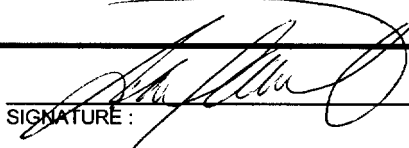
1-25-2001

Signature

Samantha Bell

Typed Name of
Person Signing

Samantha Bell

U.S. APPLICATION NO. (IF KNOWN) 09/744531		INTERNATIONAL APPLICATION NO. PCT/IB99/01326		ATTORNEY'S DOCKET NUMBER 12683-003001	
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860.00	
Surcharge of \$130 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$0.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	26 - 20 =	6	x \$18	\$108.00	
Independent Claims	4 - 3 =	1	x \$80	\$80.00	
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			+ \$270	\$270.00	
TOTAL OF ABOVE CALCULATIONS =				\$1,318.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$1,318.00	
Processing fee of \$130 for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0.00	
TOTAL NATIONAL FEE =				\$1,318.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$0.00	
TOTAL FEES ENCLOSED =				\$1318.00	
				Amount to be refunded:	\$
				Charged:	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$1,318.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. 06-1050 in the amount of \$0.00 to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 06-1050. A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
Timothy A. French FISH & RICHARDSON P.C. 225 Franklin Street Boston, MA 02110-2804 (617) 542-5070 phone (617) 542-8906 facsimile			SIGNATURE:  NAME: Timothy A. French REGISTRATION NUMBER: 30,175		

SCANNED # 14

#6/a

Rec'd PCT/PTO 15 JUN 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Jacobus Philippus Van Dyk et al. Art Unit : Unknown
 Serial No. : 09/744,531 Examiner : Unknown
 Filed : January 25, 2001
 International Appl. No.: PCT/IB99/01326
 International Filing Date: 27 July 1999
 Title : BENEFICATION OF TITANIA SLAG BY OXIDATION AND REDUCTION
 TREATMENT

Commissioner for Patents
 Washington, D.C. 20231

PRELIMINARY AMENDMENT

Prior to examination, please amend the application as follows:

In the specification:

Replace the paragraph beginning at page 1, line 9 with the following rewritten paragraph:

--More particularly the process of the present invention includes the steps of sizing the slag; oxidizing the sized slag and then reducing the oxidized slag. The treated slag may then be subjected to steps such as acid leaching.--

Replace the paragraph beginning at page 2, line 9 with the following rewritten paragraph:

--Accordingly the chloride process is a more popular process and is growing in popularity. The feedstock suitable for use in the chloride process usually needs to have a high TiO₂ content and needs to contain fewer impurities than those suitable for the sulphate process.--

CERTIFICATE OF MAILING BY EXPRESS MAIL

Express Mail Label No. EL 856747759US

I hereby certify under 37 CFR §1.10 that this correspondence is being deposited with the United States Postal Service as Express Mail Post Office to Addressee with sufficient postage on the date indicated below and is addressed to the Commissioner for Trademarks, 2900 Crystal Drive, Arlington, VA 22202-3513.

June 15, 2001

Date of Deposit

Signature

Joshua Cronin
 Joshua Cronin

Typed or Printed Name of Person Signing Certificate

09744531

Replace the paragraph beginning at page 6, line 5 with the following rewritten paragraph:

--A process is described in U.S. patents 4,629,607; 4,933,153; 5,063,032 and 5,389,355 to upgrade titania slag containing at least one alkaline earth impurity. Firstly the slag is preheated in a fluidized bed reactor in an atmosphere void of oxygen to prevent the oxidation of the Ti(III) present in the slag to Ti(IV). The slag is then contacted with hydrogen chloride gas. This results in the formation of iron and alkaline earth chlorides in the slag. Finally the chlorides that formed during the chlorination treatment are leached with either water or hydrochloric acid.--

Replace the paragraph beginning at page 8, line 1 with the following rewritten paragraph:

--Patent application PCT/CA96/00767 referred to in the above paragraph also stresses the differences between the treatment of ilmenite and titania slag. In example 12 the application illustrates that the process of GB1,225,826 relating to the treatment of ilmenite (as discussed above) is not suitable when applied to titania slag. As in the case of the process of PCT/CA96/00767, the process of GB1,225,826 includes an oxidation and subsequent reduction treatment. However, negligible removal of impurities are achieved when the process of GB1,225,826 is applied to slag, that is by oxidizing the slag with air at 850°C for 2 hours and then reducing it with smelter gas at 850°C for 5 minutes and thereafter leaching the resulting product with a hydrochloric acid solution under reflux conditions. Even if the process is modified by carrying out the oxidation at 900°C for 1 hour and the reduction at 900°C for 30 minutes (as set out in example 13 of PCT/CA96/00767) very poor results are achieved.--

Replace the paragraph beginning at page 8, line 19 with the following rewritten paragraph:

--Most surprising it has now been found that if titania slag is oxidized at a lower temperature than that described in patent application PCT/CA96/00767 under the correct conditions and thereafter reduced and further treated, the slag can be suitably upgraded. In some embodiments of the invention it is not necessary to carry out the leaching at above atmospheric pressure. Leaching at a pressure above atmospheric pressure is required in the process of

PCT/CA96/00767. It will be appreciated that even if leaching at above atmospheric pressure may not be necessary for the successful beneficiation of titania slag according to the invention, the process will also function if acid leaching is carried out at above atmospheric pressure.--

Replace the paragraph beginning at page 9, line 13 with the following rewritten paragraph:

--According to the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.--

Replace the paragraph beginning at page 10, line 3 with the following rewritten paragraph:

--According to another aspect of the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) stage; and

- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) stage.--

Replace the paragraph beginning at page 11, line 3 with the following rewritten paragraph:

--During the oxidation step the iron present in the slag preferably concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilize in the slag.--

Replace the paragraph beginning at page 11, line 10 with the following rewritten paragraph:

--The oxidation is preferably carried out in a fluidized bed reactor.--

Replace the paragraph beginning at page 11, line 11 with the following rewritten paragraph:

--The oxidizing atmosphere may comprise oxygen diluted by an inert gas (preferably a mixture of CO_2 and N_2) containing at least 2% oxygen by volume. More preferably the atmosphere results from the combustion of a carbonaceous fuel with excess air. Most preferably the oxidizing atmosphere contains between 4% and 8% oxygen by volume.--

Replace the paragraph beginning at page 11, line 15 with the following rewritten paragraph:

--Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidizing of the slag. The reduction is preferably carried out at a temperature between about 800°C and about 875°C.--

Replace the paragraph beginning at page 11, line 19 with the following rewritten paragraph:

--The reduction is preferably carried out in a fluidized bed reactor.--

Replace the paragraph beginning at page 12, line 11 with the following rewritten paragraph:

--According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO_2 content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950° for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO_2 content and leach liquor containing the leached impurities.--

Replace the paragraph beginning at page 13, line 5 with the following rewritten paragraph:

--According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO_2 content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidizing the sized slag particles oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase phase to stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;

- reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.--

Replace the paragraph beginning at page 15, line 11 with the following rewritten paragraph:

--Preferred embodiments of the invention will now be described by way of example only and with reference to the accompanying drawings wherein:

Figure 1 is a X-ray diffraction pattern of as-cast titania slag;

Figure 2 is a X-ray diffraction pattern of oxidized titania slag;

Figure 3 is a X-ray diffraction pattern of oxidized and reduced titania slag;

Figure 4 is a X-ray diffraction pattern of oxidized and reduced titania slag after leaching;

and

Figure 5 is a chemical composition profile through a titania slag particle oxidized for 1 hour at 850°C in 8% oxygen.

Replace the paragraph beginning at page 16, line 4 with the following rewritten paragraph:

--As described above titania slag is formed by smelting ilmenite ore in an electric arc furnace to form pig iron and titania rich slag. The titania rich slag is cast in a molten state into ladles whereby solid blocks are produced ranging from a few tons to as much as forty tons. Titania slag mainly consists of a pseudobrookite solid solution phase also known as the M₃O₅ solid solution. The solid solution phase with general formula (Fe²⁺, Mg²⁺, Mn²⁺, Ti⁴⁺, Ti³⁺)₃ O₅ contains iron in the Fe(II) state, titanium in the Ti(III) and (IV) states. Potentially it can also contain iron in the Fe(III) state but then titanium in the Ti(III) state will not be present. Chemically the M₃O₅ phase contains 81 to 91% TiO₂ and between 5% and 13% FeO. The M₃O₅ phase occurs as fine to coarse grained, angular to sub-rounded greyish coloured particles with a

smooth appearance. Small amounts of a silicate-rich glass can also be found, situated at the grain-and crystal boundaries of the individual M_3O_5 crystals. This glass contains a second silicate-enriched glass. The silicate-enriched glassy phase has a smooth appearance and contains finely disseminated metallic iron spheroids and droplets. The major glassy phase is fine crystalline, containing fine needle-like titanium oxide crystallites as well as fine metallic iron particles and coarser-grained "globules". The larger metallic "globules" are characterized by an iron sulphide-containing outer rim. In most instances the slag may also contain small amounts of rutile.--

Replace the paragraph beginning at page 17, line 18 with the following rewritten paragraph:

--The crushing and sizing of the titania slag is followed by an oxidation procedure. This is conducted by reacting the sized slag at a temperature between 700°C and 950°C, preferably between 800°C and 875°C with an oxidizing atmosphere for ½ to 4 hours. A fluid bed reactor is preferred for this procedure, while the oxidizing gas is preferably oxygen diluted by an inert gas (such as N_2) to levels containing between 2% and 12% O_2 .--

Replace the paragraph beginning at page 18, line 4 with the following rewritten paragraph:

--An optical microscopic investigation conducted on polished blocks of the oxidized samples revealed that major changes in the general appearance, as well as mineralogical composition of the as-cast slag occurred during the oxidation process. Pores formed and slag particles lost their "smooth" appearance to become zoned. Some of the larger particles had unoxidized M_3O_5 cores surrounded by a TiO_2 -rich intermediate zone. Most of the smaller particles were transformed to TiO_2 . The TiO_2 phases that formed were a mixture of anatase and rutile. On the outside edges of all the particles were iron-enriched, slightly porous marginal zones. Figure 5 provides evidence of the iron enriched outside edge. Limited iron migration towards the edges of cracks also occurred. Inside the unoxidized M_3O_5 cores of the slag particles fine metallic iron particle, situated at the edges of fine cracks extending through the slag

particles, could be observed. Most of the iron is converted to the Fe(III) state and all of the titanium is present in the Ti(IV) state.--

Replace the paragraph beginning at page 19, line 5 with the following rewritten paragraph:

--Reduction of the oxidized titania slag

The next step is to reduce the oxidized slag. This is conducted by contacting the oxidized slag particles with a reducing agent at a temperature from about 700°C to about 950°C, preferably between about 800°C and about 875°C, preferably in a fluidized bed reactor. The reduction is carried out for a period of at least 20 minutes.--

Replace the paragraph beginning at page 19, line 13 with the following rewritten paragraph:

--The general optical appearance of the slag particles after reduction is very similar to those of the oxidized products except that the iron enriched outer rims of the particles are converted to ilmenite. Some of the particles can be coated with a thin layer of carbon. Most, but not all of the iron is converted to the Fe(II) state and only a very small portion of the titanium is converted to the Ti(III) state.--

Replace the paragraph beginning at page 19, line 19 with the following rewritten paragraph:

--A typical X-ray diffraction pattern of titania slag that was oxidized and reduced is presented in Figure 3. This shows:

- i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;
- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;
- iii) a minor ilmenite peak (i), taken at a d-spacing of 2.754Å and a 2θ angle of 32.483° for Cu Kα radiation; and
- iv) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.--

FOR THE SLOTTED

Replace the paragraph beginning at page 20, line 10 with the following rewritten paragraph:

--After the oxidation and reduction roast the slag is leached in 20 wt% hydrochloric acid at the boiling point of the acid at atmospheric pressure or at elevated pressure. The solids are contacted with an excess of acid required to dissolve the iron and other impurity oxides. The time required for leaching will be dictated by the slag composition and the temperature used for the reaction. Optically, the leached residue displays a weathered appearance compared to the oxidized as well as reduced products. The effect of leaching is most prominent along the outer margins of the slag particles as well as along cracks extending into the individual slag particles.--

Replace the paragraph beginning at page 22, line 9 with the following rewritten paragraph:

--The slag was broken down by crushing and screened at +106 μm -850 μm . Following this the slag was oxidized in a fluidized bed reactor at 850°C for 30 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 4.--

Replace the paragraph beginning at page 23, line 4 with the following rewritten paragraph:

--The same slag as in Example 1 was broken down by crushing and screened at +106 μm -850 μm . Following this the slag was oxidized in a fluidized bed reactor at 950°C for 120 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 950°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion

of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 5.--

Replace the paragraph beginning at page 24, line 3 with the following rewritten paragraph:

--The slag was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidized in a fluidized bed reactor at 850°C for 120 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 12%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 7.--

Replace the paragraph beginning at page 24, line 14 with the following rewritten paragraph:

--The same slag as in Example 1 was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidized in a fluidized bed reactor at 705°C for 120 minutes in an oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 4%. Thereafter it was reduced in the same reactor at 750°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 8.--

Replace the paragraph beginning at page 26, line 8 with the following rewritten paragraph:

--The slag was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidized in a fluidized bed reactor at 850°C for 3 hours in an oxidizing atmosphere that resulted from the combustion of coal char in an excess of air. Thereafter it was reduced in the same reactor at 800°C for 30 minutes in a reducing atmosphere that resulted from

the combustion of coal in the absence of excess air. The roasted slag was then leached in a pressure vessel at 140°C in 20 wt% hydrochloric acid for 2 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 12.--

In the claims:

Amend claims 1, 4-6, 15, and 17-19, as follows:

- 1. (Amended) A method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of
- sizing the titania slag to a particle size from 75 to 850 μm ;
 - oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilize in the slag, allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
 - reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.--
- 4. (Amended) The method of any one of the claims 1 to 3 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidized of the slag.--
- 5. (Amended) The method of any one of the claims 1 to 3 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidizing of the slag.--
- 6. (Amended) A method of beneficiating titania slag to increase the TiO_2 content thereof to at least 90% by weight comprising the steps of:
- sizing the titania slag to a particle size from 75 to 850 μm ;
 - oxidizing the sized slag particles in an oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilize in the slag, allowing the iron present in the slag to concentrate at the exposed surfaces of

the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;

reducing the oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and

leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.--

--15. (Amended) The method of any one of claims 6 to 13 wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.--

--17. (Amended) The method of any one of claims 6 to 13 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidizing of the slag.--

--18. (Amended) The method of any one of claims 6 to 13 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidizing of the slag.--

--19. (Amended) A product when formed by a method of any one of the claims 1 to 3 and 6 to 13.--

FOR OFFICIAL USE ONLY

REMARKS

Claims 1-19 are pending in this application. Claims 1, 4-6, 15, and 17-19 have been amended herein. Claims 2, 3, 7-14, and 16 remain unchanged.

The specification, claims and abstract are all amended herein for better conformance with the requirements of U.S. practice, including for conforming the spelling. The claims are also amended to eliminate multiple dependent claims that are improper under U.S. practice.

Applicants submit that no new matter has been introduced.

Attached is a marked-up version of the changes being made by the current amendment.

Applicant asks that all claims be examined. Enclosed is a check in the amount of \$648.00 for excess claim fees. Please apply any other charges or credits to Deposit Account No. 06-1050.

Respectfully submitted,

Date:

Se 18, 2001



Timothy A. French
Reg. No. 30,175

Fish & Richardson P.C.
225 Franklin Street
Boston, MA 02110-2804
Telephone: (617) 542-5070
Facsimile: (617) 542-8906

Version with markings to show changes made

In the specification:

Paragraph beginning at page 1, line 9 has been amended as follows:

--More particularly the process of the present invention includes the steps of sizing the slag; [oxidising] oxidizing the sized slag and then reducing the [oxidised] oxidized slag. The treated slag may then be subjected to steps such as acid leaching.--

Paragraph beginning at page 2, line 9 has been amended as follows:

--Accordingly the chloride process is a more popular process and is growing in popularity. The feedstock suitable for use in the chloride process usually [need] needs to have a high TiO₂ content and [need] needs to contain fewer impurities than those suitable for the sulphate process.--

Paragraph beginning at page 6, line 5 has been amended as follows:

--A process is described in U.S. patents 4,629,607; 4,933,153; 5,063,032 and [5,384,355] 5,389,355 to upgrade titania slag containing at least one alkaline earth impurity. Firstly the slag is preheated in a [fluidised] fluidized bed reactor in an atmosphere void of oxygen to prevent the oxidation of the Ti(III) present in the slag to Ti(IV). The slag is then contacted with hydrogen chloride gas. This results in the formation of iron and alkaline earth chlorides in the slag. Finally the chlorides that formed during the chlorination treatment are leached with either water or hydrochloric acid.--

Paragraph beginning at page 8, line 1 has been amended as follows:

--Patent application PCT/CA96/00767 referred to in the above paragraph also stresses the differences between the treatment of ilmenite and titania slag. In example 12 the application illustrates that the process of GB1,225,826 relating to the treatment of ilmenite (as discussed above) is not suitable when applied to titania slag. As in the case of the process of PCT/CA96/00767, the process of GB1,225,826 includes an oxidation and subsequent reduction

treatment. However, negligible removal of impurities are achieved when the process of GB1,225,826 is applied to slag, that is by [oxidising] oxidizing the slag with air at 850°C for 2 hours and then reducing it with smelter gas at 850°C for 5 minutes and thereafter leaching the resulting product with a hydrochloric acid solution under reflux conditions. Even if the process is modified by carrying out the oxidation at 900°C for 1 hour and the reduction at 900°C for 30 minutes (as set out in example 13 of PCT/CA96/00767) very poor results are achieved.--

Paragraph beginning at page 8, line 19 has been amended as follows:

--Most surprising it has now been found that if titania slag is [oxidised] oxidized at a lower temperature than that described in patent application PCT/CA96/00767 under the correct conditions and thereafter reduced and further treated, the slag can be suitably upgraded. In some embodiments of the invention it is not necessary to carry out the leaching at above atmospheric pressure. Leaching at a pressure above atmospheric pressure is required in the process of PCT/CA96/00767. It will be appreciated that even if leaching at above atmospheric pressure may not be necessary for the successful beneficiation of titania slag according to the invention, the process will also function if acid leaching is carried out at above atmospheric pressure.--

Paragraph beginning at page 9, line 13 has been amended as follows:

--According to the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850 µm;
- [oxidising] oxidizing the sized slag particles in an [oxidising] oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III)

state to the Fe(II) state without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.--

Paragraph beginning at page 10, line 3 has been amended as follows:

--According to another aspect of the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850 μm ;
- [oxidising] oxidizing the sized slag particles in an [oxidising] oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to [stabilise] stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) stage; and
- reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) stage.--

Paragraph beginning at page 11, line 3 has been amended as follows:

--During the oxidation step the iron present in the slag preferably concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to [stabilise] stabilize in the slag.--

Paragraph beginning at page 11, line 10 has been amended as follows:

--The oxidation is preferably carried out in a [fluidised] fluidized bed reactor.--

Paragraph beginning at page 11, line 11 has been amended as follows:

--The [oxidising] oxidizing atmosphere may comprise oxygen diluted by an inert gas (preferably a mixture of CO_2 and N_2) containing at least 2% oxygen by volume. More preferably the atmosphere results from the combustion of a carbonaceous fuel with excess air. Most

preferably the [oxidising] oxidizing atmosphere contains between 4% and 8% oxygen by volume.--

Paragraph beginning at page 11, line 15 has been amended as follows:

--Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all the iron in the Fe(II) state is converted to the Fe(III) state during [oxidising] oxidizing of the slag. The reduction is preferably carried out at a temperature between about 800°C and about 875°C.--

Paragraph beginning at page 11, line 19 has been amended as follows:

--The reduction is preferably carried out in a [fluidised] fluidized bed reactor.--

Paragraph beginning at page 12, line 11 has been amended as follows:

--According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850µm;
- [oxidising] oxidizing the sized slag particles in an [oxidising] oxidizing atmosphere at a temperature from about 700°C and above but below about 950° for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.--

Paragraph beginning at page 13, line 5 has been amended as follows:

--According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO_2 content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 μm ;
- [oxidising] oxidizing the sized slag particles [oxidising] oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase phase to [stabilise] stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO_2 content and leach liquor containing the leached impurities.--

Paragraph beginning at page 15, line 11 has been amended as follows:

--Preferred embodiments of the invention will now be described by way of example only and with reference to the accompanying drawings wherein:

Figure 1 is a X-ray diffraction pattern of as-cast titania slag;

Figure 2 is a X-ray diffraction pattern of [oxidised] oxidized titania slag;

Figure 3 is a X-ray diffraction pattern of [oxidised] oxidized and reduced titania slag;

Figure 4 is a X-ray diffraction pattern of [oxidised] oxidized and reduced titania slag after leaching; and

Figure 5 is a chemical composition profile through a titania slag particle [oxidised] oxidized for 1 hour at 850°C in 8% oxygen.

Paragraph beginning at page 16, line 4 has been amended as follows:

--As described above titania slag is formed by smelting ilmenite ore in an electric arc furnace to form pig iron and titania rich slag. The titania rich slag is cast in a molten state into ladles whereby solid blocks are produced ranging from a few tons to as much as forty tons. Titania slag mainly consists of a pseudobrookite solid solution phase also known as the M_3O_5 solid solution. The solid solution phase with general formula $(Fe^{2+}, Mg^{2+}, Mn^{2+}, Ti^{4+}, Ti^{3+})_3 O_5$ contains iron in the Fe(II) state, titanium in the Ti(III) and (IV) states. Potentially it can also contain iron in the Fe(III) state but then titanium in the Ti(III) state will not be present. Chemically the M_3O_5 phase contains 81 to 91% TiO_2 and between 5% and 13% FeO. The M_3O_5 phase occurs as fine to coarse grained, angular to sub-rounded greyish coloured particles with a smooth appearance. Small amounts of a silicate-rich glass can also be found, situated at the grain-and crystal boundaries of the individual M_3O_5 crystals. This glass contains a second silicate-enriched glass. The silicate-enriched glassy phase has a smooth appearance and contains finely disseminated metallic iron spheroids and droplets. The major glassy phase is fine crystalline, containing fine needle-like titanium oxide crystallites as well as fine metallic iron particles and coarser-grained "globules". The larger metallic "globules" are [characterised] characterized by an iron sulphide-containing outer rim. In most instances the slag may also contain small amounts of rutile.--

Paragraph beginning at page 17, line 18 has been amended as follows:

--The crushing and sizing of the titania slag is followed by an oxidation procedure. This is conducted by reacting the sized slag at a temperature between 700°C and 950°C, preferably between 800°C and 875°C with an [oxidising] oxidizing atmosphere for ½ to 4 hours. A fluid bed reactor is preferred for this procedure, while the [oxidising] oxidizing gas is preferably oxygen diluted by an inert gas (such as N_2) to levels containing between 2% and 12% O_2 .--

Paragraph beginning at page 18, line 4 has been amended as follows:

--An optical microscopic investigation conducted on polished blocks of the [oxidised] oxidized samples revealed that major changes in the general appearance, as well as mineralogical composition of the as-cast slag occurred during the oxidation process. Pores formed and slag

particles lost their "smooth" appearance to become zoned. Some of the larger particles had unoxidized M_3O_5 cores surrounded by a TiO_2 -rich intermediate zone. Most of the smaller particles were transformed to TiO_2 . The TiO_2 phases that formed were a mixture of anatase and rutile. On the outside edges of all the particles were iron-enriched, slightly porous marginal zones. Figure 5 provides evidence of the iron enriched outside edge. Limited iron migration towards the edges of cracks also occurred. Inside the unoxidized M_3O_5 cores of the slag particles fine metallic iron particle, situated at the edges of fine cracks extending through the slag particles, could be observed. Most of the iron is converted to the Fe(III) state and all of the titanium is present in the Ti(IV) state.--

Paragraph beginning at page 19, line 5 has been amended as follows:

--Reduction of the [oxidised] oxidized titania slag

The next step is to reduce the [oxidised] oxidized slag. This is conducted by contacting the [oxidised] oxidized slag particles with a reducing agent at a temperature from about 700°C to about 950°C, preferably between about 800°C and about 875°C, preferably in a [fluidised] fluidized bed reactor. The reduction is carried out for a period of at least 20 minutes.--

Paragraph beginning at page 19, line 13 has been amended as follows:

--The general optical appearance of the slag particles after reduction is very similar to those of the [oxidised] oxidized products except that the iron enriched outer rims of the particles are converted to ilmenite. Some of the particles can be coated with a thin layer of carbon. Most, but not all of the iron is converted to the Fe(II) state and only a very small portion of the titanium is converted to the Ti(III) state.--

Paragraph beginning at page 19, line 19 has been amended as follows:

--A typical X-ray diffraction pattern of titania slag that was [oxidised] oxidized and reduced is presented in Figure 3. This shows:

i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu K α radiation;

ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;

iii) a minor ilmenite peak (i), taken at a d-spacing of 2.754Å and a 2θ angle of 32.483° for Cu Kα radiation; and

iv) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.--

Paragraph beginning at page 20, line 10 has been amended as follows:

--After the oxidation and reduction roast the slag is leached in 20 wt% hydrochloric acid at the boiling point of the acid at atmospheric pressure or at elevated pressure. The solids are contacted with an excess of acid required to dissolve the iron and other impurity oxides. The time required for leaching will be dictated by the slag composition and the temperature used for the reaction. Optically, the leached residue displays a weathered appearance compared to the [oxidised] oxidized as well as reduced products. The effect of leaching is most prominent along the outer margins of the slag particles as well as along cracks extending into the individual slag particles.--

Paragraph beginning at page 22, line 9 has been amended as follows:

--The slag was broken down by curshing and screened at +106 μm-850 μm. Following this the slag was [oxidised] oxidized in a [fluidised] fluidized bed reactor at 850°C for 30 minutes in an [oxidising] oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmospere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficated titania slag is given in Table 4.--

Paragraph beginning at page 23, line 4 has been amended as follows:

--The same slag as in Example 1 was broken down by crushing and screened at +106 μm-850 μm. Following this the slag was [oxidised] oxidized in a [fluidised] fluidized bed reactor at

950°C for 120 minutes in an [oxidising] oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 950°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 5.--

Paragraph beginning at page 24, line 3 has been amended as follows:

--The slag was broken down by crushing and screened at +106 µm-850 µm. Following this the slag was [oxidised] oxidized in a [fluidised] fluidized bed reactor at 850°C for 120 minutes in an [oxidising] oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 12%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 7.--

Paragraph beginning at page 24, line 14 has been amended as follows:

--The same slag as in Example 1 was broken down by crushing and screened at +106 µm-850 µm. Following this the slag was [oxidised] oxidized in a [fluidised] fluidized bed reactor at 705°C for 120 minutes in an [oxidising] oxidizing atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 4%. Thereafter it was reduced in the same reactor at 750°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 8.--

Paragraph beginning at page 26, line 8 has been amended as follows:

--The slag was broken down by crushing and screened at +106 μm -850 μm . Following this the slag was [oxidised] oxidized in a [fluidised] fluidized bed reactor at 850°C for 3 hours in an [oxidising] oxidizing atmosphere that resulted from the combustion of coal char in an excess of air. Thereafter it was reduced in the same reactor at 800°C for 30 minutes in a reducing atmosphere that resulted from the combustion of coal in the absence of excess air. The roasted slag was then leached in a pressure vessel at 140°C in 20 wt% hydrochloric acid for 2 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 12.--

In the claims:

Claims 1, 4-6, 15 and 17-19 have been amended, as follows:

--1. (Amended) A method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of

sizing the titania slag to a particle size from 75 to 850 μm ;

[oxidising] oxidizing the sized slag particles in an [oxidising] oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to [stabilise] stabilize in the slag, allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and

reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.--

--4. (Amended) The method of any one of the [preceding] claims 1 to 3 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during [oxidising] oxidized of the slag.--

--5. (Amended) The method of any one of the [preceding] claims 1 to 3 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during [oxidising] oxidizing of the slag.--

--6. (Amended) A method of beneficiating titania slag to increase the TiO₂ content thereof to at least 90% by weight comprising the steps of:

sizing the titania slag to a particle size from 75 to 850 µm;

[oxidising] oxidizing the sized slag particles in an [oxidising] oxidizing atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to [stabilise] stabilize in the slag, allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;

reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and

leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.--

--15. (Amended) The method of any one of claims 6 to [14] 13 wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.--

--17. (Amended) The method of any one of claims 6 to [16] 13 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during [oxidising] oxidizing of the slag.--

--18. (Amended) The method of any one of claims 6 to [17] 13 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during [oxidising] oxidizing of the slag.--

FILED "T E C H N I C A L"

--19. (Amended) A product when formed by a method of any one of the [preceding] claims 1 to 3 and 6 to 13.--

In the abstract:

--This invention relates to a method of treating titania slag to increase the leachability of impurities from the slag [comprising] consisting of the steps of sizing the titania slag to a particle size from 75 to 850 μm ; [oxidising] oxidizing the sized slag particles at a temperature from about 700°C and above but below about 950°C allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles and/or allowing an anatase phase to [stabilise] stabilize in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and reducing the [oxidised] oxidized slag in a reducing atmosphere from about 700°C to about 950°C to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state. The invention also relates to a method of [beneficiating] beneficiating titania slag to increase the TiO_2 content thereof wherein the above treated slag is leached with acid.--

TO 30 " T E 30 30

09/744531
500 Rec'd PCT/PTO 2 5 JAN 2001

APPLICATION
FOR
UNITED STATES LETTERS PATENT

TITLE: BENEFICATION OF TITANIA SLAG BY OXIDATION
AND REDUCTION TREATMENT

APPLICANT: JACOBUS PHILIPPUS VAN DYK, NANNE MATTHEUS
VEGTER, CORNELIA PETRONELLA VISSER, THOMAS
DE LANGE, JOHN DAVID WINTER, ERNEST ALAN
WALPONE AND JOHANNES NELL

CERTIFICATE OF MAILING BY EXPRESS MAIL

Express Mail Label No. EL 224700949US

I hereby certify under 37 CFR §1.10 that this correspondence is being deposited with the United States Postal Service as Express Mail Post Office to Addressee with sufficient postage on the date indicated below and is addressed to the Commissioner for Patents, Washington, D.C. 20231

1/25-2001
Date of Deposit

Samantha Bell
Signature

Samantha Bell
Typed or Printed Name of Person Signing Certificate

**BENEFICATION OF TITANIA SLAG BY OXIDATION
AND REDUCTION TREATMENT**

1. Field of the Invention

This invention relates to a method of beneficiating titania slag to a high grade titanium dioxide (TiO_2) product. Preferably the product is suitable for use as a feedstock in titanium dioxide pigment production or titanium metal production by means of the chloride process. The invention also relates to a process for preparing intermediate products suitable for use in the beneficiation of titania slag and also to intermediate products and final products formed by the processes.

More particularly the process of the present invention includes the steps of sizing the slag; oxidising the sized slag and then reducing the oxidised slag. The treated slag may then be subjected to steps such as acid leaching.

2. Background of the Invention

Commercial uses of TiO_2

Titanium is widely known for its use as a metal, but the primary use of titanium is in the form of titanium dioxide (TiO_2). TiO_2 is used as a white pigment in paints, plastics and paper. Two types of pigment with a tetragonal crystal structure are produced, namely rutile and anatase. Rutile is preferred in outdoor paints and anatase is preferred in indoor paints.

TiO₂ pigment production

There are two commercial processes for the production of TiO₂ pigment namely, the sulphate process and the chloride process. A sulphate process plant is easier to operate and monitor than a chloride process plant, and is capable of using feedstock with a relatively low TiO₂ content. However, capital costs of a modern sulphate process plant can be higher than that of a chloride process plant of the same pigment capacity. Furthermore there is a higher volume of waste products to be treated and disposed of due to the use of more impure feedstock and the fact that the sulphate used in the process cannot be easily recovered and recycled.

Accordingly the chloride process is a more popular process and is growing in popularity. The feedstock suitable for use in the chloride process usually need to have a high TiO₂ content and need to contain fewer impurities than those suitable for the sulphate process.

TiO₂ bearing deposits

TiO₂ is commonly found in nature in the form of ilmenite (FeO. TiO₂) which contains from 40% to 80% TiO₂. Most deposits being mined produce concentrates with a TiO₂ content between 45% and 67%. Rutile deposits are far more scarce than ilmenite and they contain about 95% TiO₂ in crystalline form and are therefore of sufficient quality to be used directly in the chloride process for TiO₂ pigment production. Deposits of anatase have been discovered but have not yet been commercially exploited. Anatase typically has a TiO₂ content in excess of 95%. Leucoxene, a weathered form of ilmenite, contains up to 85% TiO₂ and is exploited on a limited commercial scale. Brookite (rhombic TiO₂), perovskite, (CaTiO₂), sphene (CaTiSiO₅) and geikielite (MgTiO₃) also contain titanium.

Beneficiation of ilmenite

Although natural rutile is suitable for use as a feedstock in the chloride process, the ever-decreasing availability of natural rutile forced chloride process pigment producers to consider other lower grade feedstock. One such alternative is naturally occurring ilmenite. Due to its relatively low TiO_2 content several processes have as their aim the upgrading of the TiO_2 content of ilmenite.

These processes include:

- i) Partial reduction of the iron in the ilmenite.

This process is described in US patents 4,038,364 and 4,199,552. In this process ilmenite is reduced at elevated temperatures to convert iron in the ferric state, (Fe(III)), to the ferrous state, (Fe(II)). This renders the iron more amenable to acid leaching of the ilmenite during upgrading of the ilmenite.

- ii) Pre-oxidation followed by partial reduction of the iron in the ilmenite.

In a process described in GB1,225,826 the ilmenite is subjected to an oxidation treatment to convert substantially all the iron to the ferric state. The ore is then reduced to convert the iron back to the ferrous state and metallic state. In the examples of the patent the oxidation is carried out at 870°C for two hours. The reduction is carried out at 870°C for five minutes. The ore exhibits the original X-ray diffraction pattern of ilmenite after treatment but is more amenable to acid leaching to upgrade the ilmenite.

- iii) Pre - oxidation followed by reduction of the iron to metallic state.

US patent 4,097,574 describes a process whereby ilmenite is subjected to an oxidation treatment to convert the iron in the ilmenite to the ferric state. Reduction treatment is then carried out to reduce the iron to metallic iron. The iron is then removed by leaching thereby to upgrade the ilmenite.

- iv) Smelting of the ore.

Ilmenite ore can also be smelted in the presence of a carbonaceous reducing agent in an electric arc furnace. This process is described in US patent 2,680,681. Two saleable products result from this namely, high quality pig iron and titania rich slag.

The slag typically contains 80 - 85% TiO_2 .

Differences between ilmenite ore and titania slag

All of the processes listed above are aimed at beneficiating ilmenite or similar titanium ores. None of these processes were applied to titania slag and there are certain fundamental differences between ilmenite ore and titania slag.

- i) The first difference is that ilmenite is a naturally occurring titanium bearing ore, while titania slag is produced by electro-smelting of ilmenite in an electric arc furnace.
- ii) The second difference can be found in the amount of the main components that are present. Ilmenite typically contains around 50% titanium oxide and around 45% iron oxide. All the titanium is present as Ti(IV) while around 20% of the iron occurs as Fe(III) and the rest is in the Fe(II) state. Titania slag typically contains around 85%

titanium oxide and around 10% iron oxide. In this instance the titanium is in the Ti(III) and the Ti(IV) state, while most of the iron is present as Fe(II).

- iii) The third difference lies in the respective mineralogical compositions. In ilmenite concentrates the iron and the titanium is organised into hexagonal ilmenite crystals.

As-cast titania slag consists of the following four phases:

- a) The most abundant phase is a crystalline phase, known as pseudobrookite or the M_3O_5 phase. This phase is a solid solution of iron oxide and titanium oxide, with the end members being $(Ti,Fe,Al,Cr,V)_2O_3.TiO_2$ and $(Mg,Mn,Fe)O.2TiO_2$ and can accommodate the main oxidation states of iron and titanium in its structure, namely Fe(II), Fe(III), Ti(III) and Ti(IV);
- b) Rutile (TiO_2) although not always present in such quantities that allows detection thereof by X-ray diffraction analysis;
- c) An amorphous, glassy phase consisting mainly of SiO_2 , TiO_2 , FeO , CaO and Al_2O_3 and;
- d) Finely disseminated metallic iron globules present in the grain boundaries of the rutile crystals and in the silicate-rich glassy matrix.

The pseudobrookite and amorphous glassy phases are characteristic of titania slag and generally do not occur in ilmenite ores. The presence of pseudobrookite and the glassy phases in titania slag may be one of the causes that the processes for beneficiating ilmenite ore are in some cases not applicable to the beneficiation of titania slag. The different compositions of slags may also play a role.

Beneficiation of titania slag

Several known processes have as their aim the upgrading of the TiO_2 content of titania slag.

These processes can be classified as follows:

i) Chlorination of the impurities

5 A process is described in US patents 4,629,607; 4,933,153; 5,063,032 and 5,384,355 to upgrade titania slag containing at least one alkaline earth impurity. Firstly the slag is preheated in a fluidised bed reactor in an atmosphere void of oxygen to prevent the oxidation of the Ti(III) present in the slag to Ti(IV). The slag is then contacted with hydrogen chloride gas. This results in the formation of iron and alkaline earth chlorides in the slag. Finally the chlorides that formed during the chlorination treatment are leached with either water or hydrochloric acid.

10 ii) Salt roasting

In US patent 4,038,363 a process for the upgrading of slag is described. The process consists of a roast procedure in the presence of an alkaline salt such as sodium chloride. After the roast procedure the agglomerates that have formed are dispersed with wet grinding. Thereafter the slag is subjected to leaching in either water or a sulphuric acid solution.

15 iii) Fluxing of the impurities

20 Titania slag can also be upgraded by heating the slag in the presence of a glass forming fluxing agent such as phosphorus pentoxide as is described in US patent 3,996,332. According to South African patent 93/5922 other glass forming agents such as the oxides of sodium, potassium, silicon etc. can also be used. After the

fluxing procedure the slag consists of a crystalline rutile phase and a glassy phase that contains most of the impurities present in the slag. Finally the slag is subjected to leaching in a mineral acid to remove the glass phase and associated impurities.

iv) Sulphatising

US patent 4,362,557 describes a process where the TiO_2 content of titania slag is increased in a two stage procedure. Firstly the slag is mixed with an alkaline salt such as sodium carbonate and reacted with either SO_3 or mixtures of SO_2 and O_2 at 700 to 1100°C. Secondly the sulphates that formed during the roasting are leached with either water or hydrochloric acid at room temperature.

v) Oxidation-reduction roasting

The process described in patent application PCT/CA96/00767 has as its basis an oxidation roast followed by a reduction roast. The slag is first sized in the range 75-850 μm and is then oxidised at a temperature of at least about 950°C, but preferably between 1000 and 1100°C, for at least 20 minutes. The oxidation procedure converts the Fe(II) and Ti(III) present in the slag to Fe(III) and Ti(IV) respectively and aims to decompose the glassy phase. After the oxidation the slag is reduced at a temperature of at least about 700°C, but preferably between 800 and 850°C, for at least 30 minutes, but preferably for a period of 1,5 to 2 hours, to convert the Fe(III) in the slag back to Fe(II). A MgO rich ilmenite-geikielite solid solution forms during the process, which is more amenable to leaching than the original phases present in the slag. The roasted titania slag is then leached under pressure in excess of atmospheric pressure and at a temperature of at least 125°C to remove the impurities present in the slag.

Patent application PCT/CA96/00767 referred to in the above paragraph also stresses the differences between the treatment of ilmenite and titania slag. In example 12 the application illustrates that the process of GB1,225,826 relating to the treatment of ilmenite (as discussed above) is not suitable when applied to titania slag. As in the case of the process of PCT/CA96/00767, the process of GB1,225,826 includes an oxidation and subsequent reduction treatment. However, negligible removal of impurities are achieved when the process of GB1,225,826 is applied to slag, that is by oxidising the slag with air at 850°C for 2 hours and then reducing it with smelter gas at 850°C for 5 minutes and thereafter leaching the resulting product with a hydrochloric acid solution under reflux conditions. Even if the process is modified by carrying out the oxidation at 900°C for 1 hour and the reduction at 900°C for 30 minutes (as set out in example 13 of PCT/CA96/00767) very poor results are achieved.

Patent application PCT/CA96/00767 teaches that the titania slag requires a pre-treatment within an unexpected window of process conditions to render it suitable for acid leaching. The patent describes much harsher oxidation, reduction and acid leaching steps for slag than the conditions for ilmenite as disclosed in the related process of GB1,225,826.

Most surprising it has now been found that if titania slag is oxidised at a lower temperature than that described in patent application PCT/CA96/00767 under the correct conditions and thereafter reduced and further treated, the slag can be suitably upgraded. In some embodiments of the invention it is not necessary to carry out the leaching at above atmospheric pressure. Leaching at a pressure above atmospheric pressure is required in the process of PCT/CA96/00767. It will be appreciated that

even if leaching at above atmospheric pressure may not be necessary for the successful beneficiation of titania slag according to the invention, the process will also function if acid leaching is carried out at above atmospheric pressure.

Patent application PCT/CA96/00767 teaches that during that process the iron cations tend to concentrate around pores formed in the slag particles which will render them more accessible to leaching. It is believed that if the oxidation step is carried out at lower temperatures as disclosed for the present invention the iron in the slag particles surprisingly migrates to the rims of the slag particles. It is believed that such slag particles undergo rapid reduction roasting and that such slag particles are more amenable to acid leaching which allows leaching to be conducted at atmospheric pressure.

3. Summary of the Invention

According to the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II)

state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.

According to another aspect of the present invention a method of treating titania slag to increase the leachability of the slag comprises the steps of

- 5 • sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700 °C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
- 10 • reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes, to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state.

15 The titania slag includes a pseudobrookite phase and a glassy phase. The glassy phase may consist mainly of SiO_2 , TiO_2 , FeO and Al_2O_3 .

The titania slag may contain titanium oxide and impurities including at least one compound selected from the group consisting of iron oxide, silicon oxide, aluminium oxide, alkaline earth oxide, manganese oxide, chromium oxide and vanadium oxide. The titanium oxide and

20 impurities may be provided in a pseudobrookite phase and a glassy phase. The alkaline earth oxide may comprise calcium oxide and/or magnesium oxide.

The titania slag is preferably crushed and preferably to a particle range of above 106 μm up to 850 μm .

During the oxidation step the iron present in the slag preferably concentrates at the exposed surfaces of the slag, and an anatase phase is allowed to stabilise in the slag.

- 5 The oxidation is preferably carried out at a temperature from about 750°C and above but preferably below about 900°C and more preferably it is carried out at a temperature from about 800°C to about 875°C.

The oxidation is carried out for longer than 30 minutes. Preferably it is carried out for a period of about 2 hours.

- 10 The oxidation is preferably carried out in a fluidised bed reactor.

The oxidising atmosphere may comprise oxygen diluted by an inert gas (preferably a mixture of CO_2 and N_2) containing at least 2% oxygen by volume. More preferably the atmosphere results from the combustion of a carbonaceous fuel with excess air. Most preferably the oxidising atmosphere contains between 4% and 8% oxygen by volume.

- 15 Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag. The reduction is preferably carried out at a temperature between about 800°C and about 875°C.

The reduction is preferably carried out in a fluidised bed reactor.

- 20 The reducing atmosphere may be supplied by any one of the following reducing agents: carbon monoxide gas, hydrogen gas, gases such as reformed natural gas and smelter off gas

and mixtures between these gases. More preferably the reducing atmosphere is supplied by the products resulting from combustion of coal.

The reduction is preferably carried out for a period of longer than 10 minutes and less than 1 hour. More preferably it is carried out for a period of 20 minutes.

5

Preferably more than 60%, preferably more than 75%, more preferably more than 90% and most preferably substantially all iron in the Fe(III) state is converted to the Fe(II) state during reduction.

10 Preferably less than 90%, more preferably less than 95% and most preferably none of the titanium in the Ti(IV) state is converted to the Ti(III) state during reduction.

According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO_2 content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 μm ;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 15 700°C and above but below about 950°C for at least 30 minutes allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for 20 at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II)

state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and

- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

5 According to another aspect of the invention there is provided a method of beneficiating titania slag to increase the TiO₂ content thereof comprising the steps of:

- sizing the titania slag to a particle size from 75 to 850 µm;
- oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes, allowing an anatase phase to stabilise in the slag, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
- reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial amount of the titanium in the Ti(IV) state to the Ti(III) state; and
- leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

The leaching may be conducted under pressure in excess of atmospheric pressure.

20 Alternatively the leaching may be conducted at atmospheric pressure. Alternatively, a combination of atmospheric and pressure leaching may be used.

The acid may be heated and preferably the acid is heated to the boiling point of the acid.

The acid may comprise a mineral acid and preferably it comprises sulphuric acid or hydrochloric acid, more preferably hydrochloric acid.

The acid may be present in at least a 10% stoichiometric excess of what is needed to convert
5 leachable oxides and alkaline impurities to soluble chlorides.

The acid leaching may be done in one or more stages. If more than one stage is used then the leaching may be done in co-current or counter-current mode.

The leaching may be done in batch or continuous mode.

The method of beneficiating titania slag may optionally include a caustic leaching step after
10 the acid leaching step.

Optionally the method includes calcination of the treated slag. Prior to calcining the treated slag it may be washed and it may be dried to remove volatile by-products. The drying step may be carried out at a temperature above 100°C.

The calcination may be carried out by heating the product between 600°C and 900°C for more
15 than 30 minutes.

The method may also include an additional step of subjecting the calcined slag to a magnetic separation procedure.

The methods of beneficiating the titania slag is preferably performed to form beneficiated titania slag suitable for use as a feedstock for the chloride process of TiO₂ pigment
20 production.

The beneficiated titania slag may contain at least 90% by weight, preferably at least 94% by weight of titanium dioxide. Preferably it contains less than 1,5%, preferably less than 1% by weight of magnesium oxide. Preferably it contains less than 0,4% by weight of calcium oxide.

- 5 The invention also relates to products formed by the methods described herein above.

According to another aspect of the invention there is provided treated titania slag containing rutile, anatase and pseudobrookite.

According to yet another aspect of the present invention there is provided treated titania slag including rutile, anatase, ilmenite and pseudobrookite.

10 4. Brief Description of the Drawings

Preferred embodiments of the invention will now be described by way of example only and with reference to the accompanying drawings wherein:

Figure 1 is a X-ray diffraction pattern of as-cast titania slag;

Figure 2 is a X-ray diffraction pattern of oxidised titania slag;

- 15 **Figure 3** is a X-ray diffraction pattern of oxidised and reduced titania slag;

Figure 4 is a X-ray diffraction pattern of oxidised and reduced titania slag after leaching; and

Figure 5 is a chemical composition profile through a titania slag particle oxidised for 1 hour at 850°C in 8% oxygen.

Detailed Description of the Invention

As described above titania slag is formed by smelting ilmenite ore in an electric arc furnace to form pig iron and titania rich slag. The titania rich slag is cast in a molten state into ladles whereby solid blocks are produced ranging from a few tons to as much as forty tons. Titania slag mainly consists of a pseudobrookite solid solution phase also known as the M_3O_5 solid solution. The solid solution phase with general formula $(Fe^{2+}, Mg^{2+}, Mn^{2+}, Ti^{4+}, Ti^{3+})_3 O_5$ contains iron in the Fe(II) state, titanium in the Ti(III) and (IV) states. Potentially it can also contain iron in the Fe(III) state but then titanium in the Ti(III) state will not be present. Chemically the M_3O_5 phase contains 81 to 91% TiO_2 and between 5% and 13% FeO. The M_3O_5 phase occurs as fine to coarse grained, angular to sub-rounded greyish coloured particles with a smooth appearance. Small amounts of a silicate-rich glass can also be found, situated at the grain-and crystal boundaries of the individual M_3O_5 crystals. This glass contains a second silicate-enriched glass. The silicate-enriched glassy phase has a smooth appearance and contains finely disseminated metallic iron spheroids and droplets. The major glassy phase is fine crystalline, containing fine needle-like titanium oxide crystallites as well as fine metallic iron particles and coarser-grained "globules". The larger metallic "globules" are characterised by an iron sulphide-containing outer rim. In most instances the slag may also contain small amounts of rutile.

Table 1 shows the chemical composition of a typical titania slag that is used as feedstock to the process described in this invention. This table shows that the main impurity present in the slag is iron.

Table 1. Chemical composition of a typical titania slag, in mass percentage, used as feedstock to the process described in the current invention.

Fe ⁰	FeO	Fe ₂ O ₃	Ti ₂ O ₃	TiO ₂	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
0.21	7.65	<0.1	34.20	50.70	1.64	0.99	0.31	1.42	1.32	0.15	0.41

A typical X-ray diffraction pattern of the titania slag feedstock is presented in Figure 1. This shows: i) a main pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.52Å and a 2θ angle from 25.553° to 25.280° for Cu Kα radiation. In this specific instance rutile is present, and exhibits a main peak (r) taken at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation. In other cases rutile is not always present.

The slag is not amenable to acid leaching for removing impurities to form a TiO₂ rich upgraded slag. Accordingly the slag requires pre-treatment to render it amenable to acid leaching. The beneficiation process of titania slag accordingly includes the following steps:-

Crushing and sizing the titania slag

The blocks of titania slag are crushed and sized using conventional methods and preferably the slag is sized in the +106-850 μm particle size range which is acceptable in the chloride process for TiO₂ pigment production.

Oxidation of the sized titania slag

The crushing and sizing of the titania slag is followed by an oxidation procedure. This is conducted by reacting the sized slag at a temperature between 700°C and 950°C, preferably

between 800°C and 875°C with an oxidising atmosphere for ½ to 4 hours. A fluid bed reactor is preferred for this procedure, while the oxidising gas is preferably oxygen diluted by an inert gas (such as N₂) to levels containing between 2% and 12%O₂.

5 An optical microscopic investigation conducted on polished blocks of the oxidised samples revealed that major changes in the general appearance, as well as mineralogical composition of the as-cast slag occurred during the oxidation process. Pores formed and slag particles lost their "smooth" appearance to become zoned. Some of the larger particles had unoxidized M₃O₅ cores surrounded by a TiO₂-rich intermediate zone. Most of the smaller particles were transformed to TiO₂. The TiO₂ phases that formed were a mixture of anatase and rutile. On 10 the outside edges of all the particles were iron-enriched, slightly porous marginal zones. Figure 5 provides evidence of the iron enriched outside edge. Limited iron migration towards the edges of cracks also occurred. Inside the unoxidized M₃O₅ cores of the slag particles fine metallic iron particle, situated at the edges of fine cracks extending through the slag particles, could be observed. Most of the iron is converted to the Fe(III) state and all of the titanium is 15 present in the Ti(IV) state.

An advantage of segregation of iron towards the outer surface of the slag particles include rapid reduction roasting and ready access of the impurities to the leach solution and their rapid selective leaching.

Figure 2 shows a typical X-ray diffraction pattern for titania slag after it was subjected to the 20 oxidation procedure. This shows:

- i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;

- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation; and
- iii) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.

5 *Reduction of the oxidised titania slag*

The next step is to reduce the oxidised slag. This is conducted by contacting the oxidised slag particles with a reducing agent at a temperature from about 700°C to about 950°C, preferably between about 800°C and about 875°C, preferably in a fluidised bed reactor. The reduction is carried out for a period of at least 20 minutes.

- 10 The reducing agent may comprise any suitable conventional reducing agent such as carbon monoxide, hydrogen, natural gas etc, or a combination thereof. Preferably it comprises the gaseous products that result from the combustion of coal.

The general optical appearance of the slag particles after reduction is very similar to those of the oxidised products except that the iron enriched outer rims of the particles are converted to
15 ilmenite. Some of the particles can be coated with a thin layer of carbon. Most, but not all of the iron is converted to the Fe(II) state and only a very small portion of the titanium is converted to the Ti(III) state.

A typical X-ray diffraction pattern of titania slag that was oxidised and reduced is presented in
20 Figure 3. This shows:

- i) a main rutile peak (r) at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;
- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;
- 5 iii) a minor ilmenite peak (i), taken at a d-spacing of 2.754Å and a 2θ angle of 32.483° for Cu Kα radiation; and
- iv) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.

Leaching of the reduced titania slag

10 After the oxidation and reduction roast the slag is leached in 20 wt% hydrochloric acid at the boiling point of the acid at atmospheric pressure or at elevated pressure. The solids are contacted with an excess of acid required to dissolve the iron and other impurity oxides. The time required for leaching will be dictated by the slag composition and the temperature used for the reaction. Optically, the leached residue displays a weathered appearance compared to

15 the oxidised as well as reduced products. The effect of leaching is most prominent along the outer margins of the slag particles as well as along cracks extending into the individual slag particles.

Table 2 gives the chemical composition of the beneficiated titania slag. This shows that most of the impurities have been removed from the slag and that it now conforms to the ideal

20 specification of the chloride process.

Table 2. The chemical composition of the beneficiated titania slag, in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
94.10	1.54	1.84	0.47	0.11	0.55	0.37	0.10	0.33

Figure 4 gives the X-ray diffraction pattern of titania slag after the oxidation, reduction and leach procedures. This shows:

- 5 i) a main rutile peak (r) taken at a d-spacing of 3.247Å and a 2θ angle of 27.445° for Cu Kα radiation;
- ii) a main anatase peak (a) taken at a d-spacing of 3.52Å and a 2θ angle of 25.279° for Cu Kα radiation;
- 10 iii) a minor pseudobrookite peak (P) taken at a d-spacing of 3.483Å to 3.497Å and a 2θ angle from 25.553° to 25.449° for Cu Kα radiation.

Drying of the leached titania slag

Following the leach procedure the leach liquor and titania slag are separated in a solid-liquid separation procedure before the titania slag is washed and then dried at temperatures between 100°C and 160°C. This removes most of the volatile by-products that resulted from the
15 interaction between the mineral acid and the titania slag.

After drying the beneficiated titania slag product contains more than 90% TiO₂, preferably between 93% and 97% TiO₂, less than 4% of total iron expressed as FeO and less than 1.2% of the alkaline earth impurities MgO and CaO combined. The main phases present in the

beneficiated titania slag are rutile and anatase, while physically only the outside rims of the particles are porous and the bulk of the particles are dense.

6. Examples

Example 1

- 5 Ilmenite from a beach sand deposit was subjected to electro-smelting in a direct current (DC) arc plasma furnace. The composition of the slag produced is presented in Table 3.

Table 3. Chemical composition of titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
86.20	9.18	1.42	0.82	0.33	1.46	1.15	0.14	0.46

- The slag was broken down by crushing and screened at +106 µm-850 µm. Following this the
 10 slag was oxidised in a fluidised bed reactor at 850°C for 30 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached
 15 in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 4.

Table 4. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
94.80	2.60	1.22	0.72	0.06	0.73	0.62	0.09	0.73

Example 2

The same slag as in Example 1 was broken down by crushing and screened at +106 µm-850 µm. Following this the slag was oxidised in a fluidised bed reactor at 950°C for 120 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 8%. Thereafter it was reduced in the same reactor at 950°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 5.

Table 5. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
92.10	3.99	1.26	0.77	0.32	0.96	0.50	0.12	0.43

Example 3

Ilmenite from a beach sand deposit was smelted in a DC arc plasma furnace. The composition of the slag that was produced is presented in Table 6.

Table 6. Chemical composition of titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
69.70	24.83	3.50	0.89	0.30	1.88	1.07	0.33	0.47

The slag was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidised in a fluidised bed reactor at 850°C for 120 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 12%. Thereafter it was reduced in the same reactor at 850°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 7.

Table 7. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
90.60	6.35	2.07	0.60	0.18	0.63	0.24	0.16	0.32

Example 4

The same slag as in Example 1 was broken down by crushing and screened at +106 μ m-850 μ m. Following this the slag was oxidised in a fluidised bed reactor at 750°C for 120 minutes in an oxidising atmosphere comprising a mixture of air and carbon dioxide that set the oxygen level at 4% . Thereafter it was reduced in the same reactor at 750°C for 20 minutes in a reducing atmosphere comprising chemically pure carbon monoxide. The roasted

slag was then leached in boiling 20% hydrochloric acid at atmospheric pressure for 12 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 8.

5 **Table 8.** Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
91.70	4.17	1.31	0.84	0.09	1.05	0.89	0.11	0.46

Example 5

This example will illustrate the inertness of as-cast titania slag to the action of mineral acids.

Titania slag with the composition listed in Table 9 was crushed and sized in the range
 10 +106 µm–850 µm.

Table 9. Chemical composition of titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
87.7	10.04	1.47	1.16	0.13	0.93	1.57	0.13	0.45

This slag was leached in 20 wt% hydrochloric acid at a temperature of 95°C for 4 hours.

Following this the leach liquor was decanted and the solids were dried. The chemical analysis

15 of the leach residue is listed in Table 10.

Table 10 Chemical composition of leach residue in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
88.40	9.08	1.26	1.08	0.10	0.98	1.56	0.11	0.44

Example 6

Ilmenite from a beach sand deposit was smelted in a DC arc plasma furnace. The composition of the slag that was produced is presented in Table 11.

Table 11. Chemical composition of titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
88.70	7.92	1.64	0.99	0.31	1.42	1.32	0.15	0.41

The slag was broken down by crushing and screened at +106 µm-850 µm. Following this the slag was oxidised in a fluidised bed reactor at 850°C for 3 hours in an oxidising atmosphere that resulted from the combustion of coal char in an excess of air. Thereafter it was reduced in the same reactor at 800°C for 30 minutes in a reducing atmosphere that resulted from the combustion of coal in the absence of excess air. The roasted slag was then leached in a pressure vessel at 140°C in 20 wt% hydrochloric acid for 2 hours. At the conclusion of the leach procedure the leach solution was decanted and the solids were washed and dried at 150°C. The composition of the beneficiated titania slag is given in Table 12.

Table 12. Composition of beneficiated titania slag in mass percentage

TiO ₂	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	V ₂ O ₅
94.6	1.82	2.03	0.40	0.14	0.40	0.30	0.09	0.29

It will be appreciated that many variations in detail are possible without thereby departing from the scope and spirit of the invention.

5

10

15

08. 08. 2000

CLAIMS

(90)

2000/08/08
PCT/IB99/01326
2000/08/08

1. A method of treating titania slag to increase the leachability of impurities from the slag comprising the steps of
 - sizing the titania slag to a particle size from 75 to 850 μm ;
 - oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilise in the slag, allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state; and
 - reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state.
2. The method of claim 1 wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.
3. The method of claim 2 wherein the oxidation is carried out at a temperature from about 800°C to about 875°C.

WO 00/06786

PCT/IB99/01326

4. The method of any one of the preceding claims wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.
5. The method of any one of the preceding claims wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.
6. A method of beneficiating titania slag to increase the TiO₂ content thereof to at least 90% by weight comprising the steps of:
 - sizing the titania slag to a particle size from 75 to 850 µm;
 - oxidising the sized slag particles in an oxidising atmosphere at a temperature from about 700°C and above but below about 950°C for at least 30 minutes allowing an anatase phase to stabilise in the slag, allowing the iron present in the slag to concentrate at the exposed surfaces of the slag particles, allowing a major portion of the iron in the Fe(II) state to convert to the Fe(III) state, and allowing the titanium in the Ti(III) state to be converted to the Ti(IV) state;
 - reducing the oxidised slag in a reducing atmosphere from about 700°C to about 950°C for at least 5 minutes to convert a major portion of the iron in the Fe(III) state to the Fe(II) state and without converting a substantial portion of the titanium in the Ti(IV) state to the Ti(III) state; and
 - leaching the reduced slag with acid to obtain a beneficiated slag product with an increased TiO₂ content and leach liquor containing the leached impurities.

WO 00/06786

PCT/IB99/01326

7. The method of claim 6 wherein the leaching is conducted under pressure in excess of atmospheric pressure.
8. The method of claim 6 wherein the leaching is conducted at atmospheric pressure.
9. The method of claim 6 wherein the acid used in the leaching step is heated.
10. The method of claim 6 wherein the acid used in the leaching step comprises hydrochloric acid.
11. The method of claim 6 which includes a caustic leaching step after the acid leaching step.
12. The method of claim 6 which includes a step of calcining the treated slag.
13. The method of claim 12 wherein the treated slag is washed and dried to remove volatile by products prior to the calcining step.

WO 00/06786

PCT/IB99/01326

14. The method of either one of claims 12 or 13 wherein the calcined slag is subjected to a magnetic separation procedure.
15. The method of any one of claims 6 to 14 wherein the oxidation is carried out at a temperature from about 750°C and above but below about 900°C.
16. The method of claim 15 wherein the oxidation is carried out at a temperature from about 800°C to about 875°C.
17. The method of any one of claims 6 to 16 wherein more than 90% of the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.
18. The method of any one of claims 6 to 17 wherein substantially all the iron in the Fe(II) state is converted to the Fe(III) state during oxidising of the slag.
19. A product when formed by a method of any one of the preceding claims.

TOP SECRET

WO 00/06786

09/744531

PCT/IB99/01326

1/5

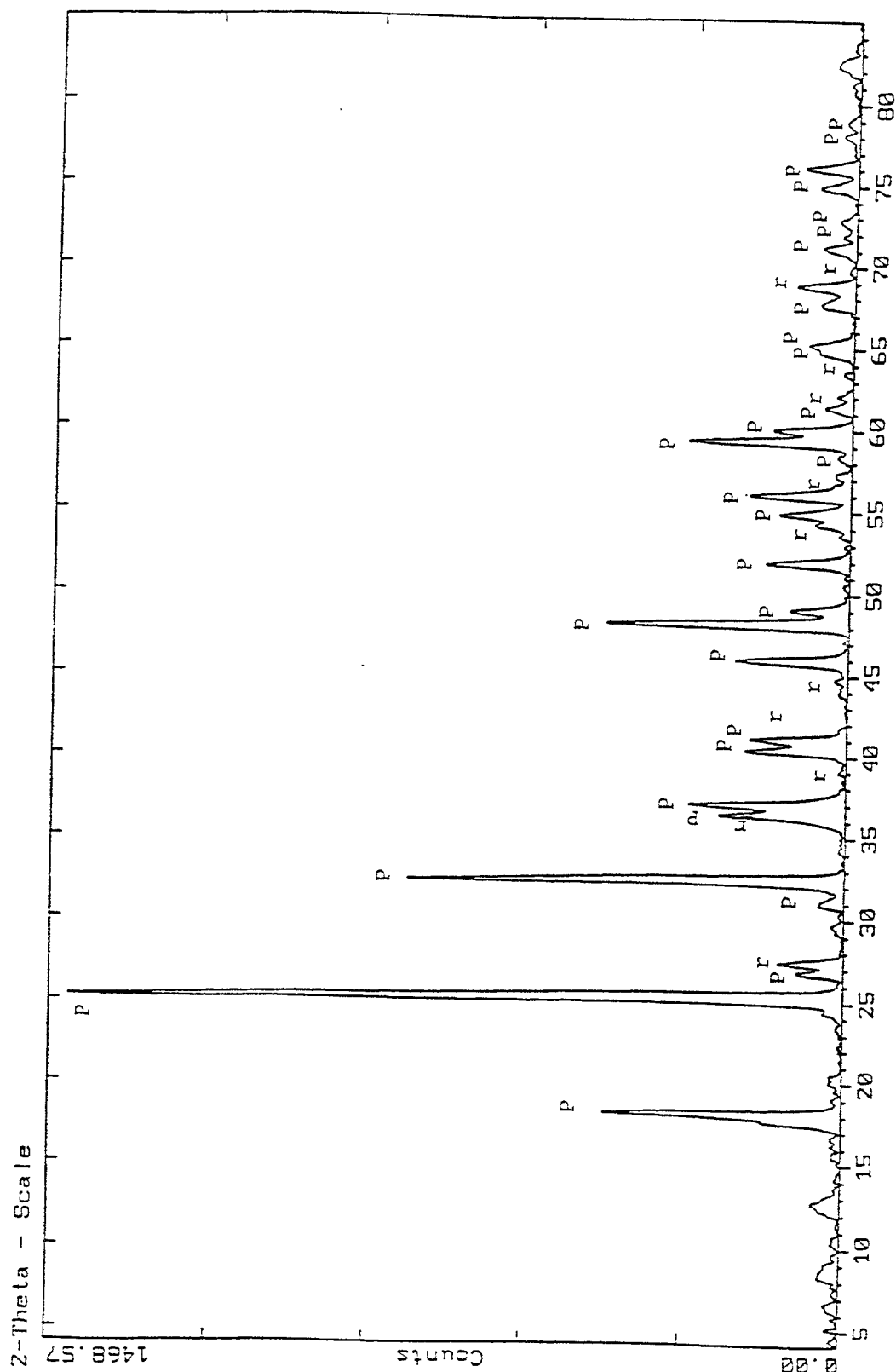


Figure 1

09/744531

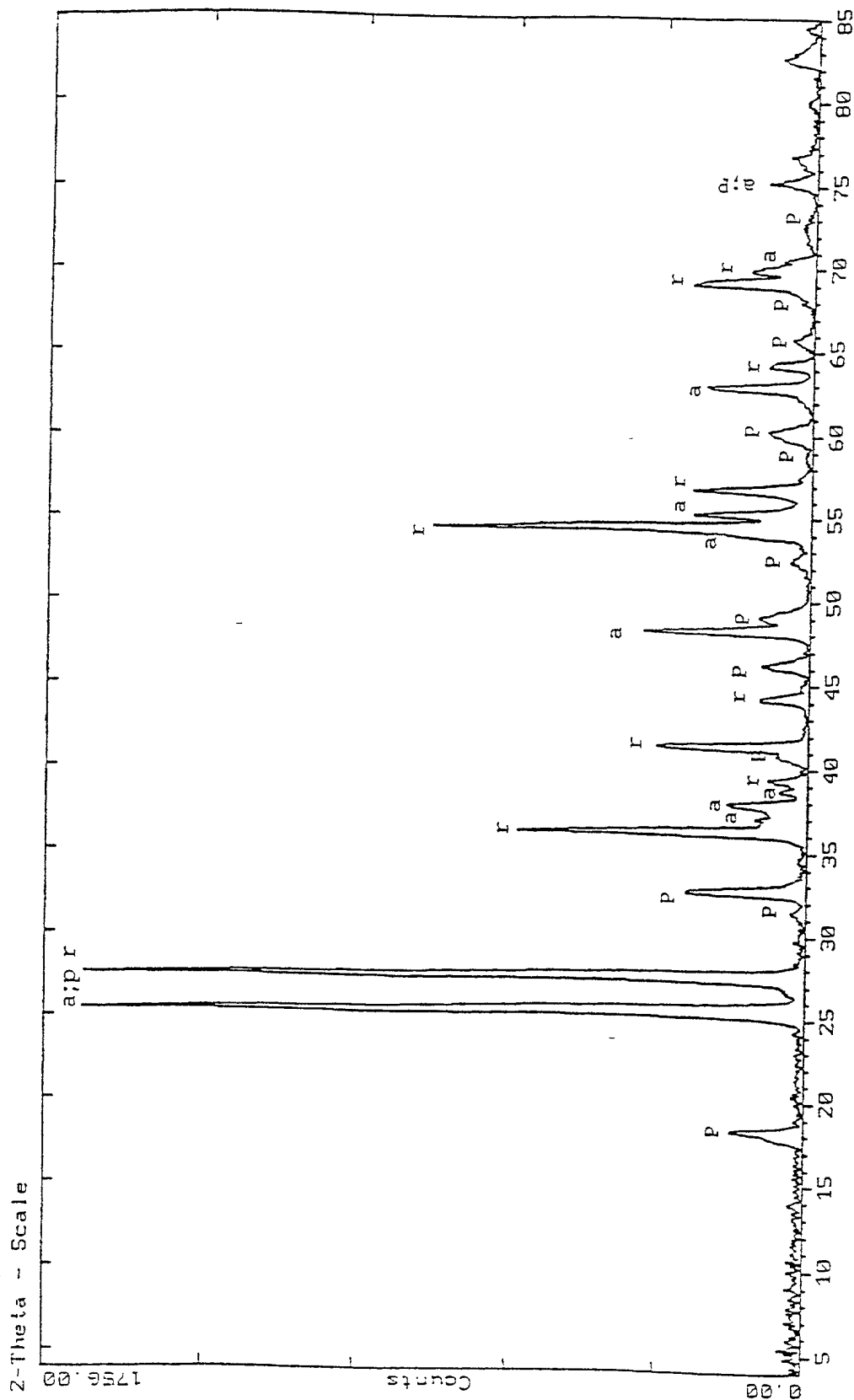


Figure 2

FOI 90-1544260

WO 00/06786

09/744531

PCT/IB99/01326

3/5

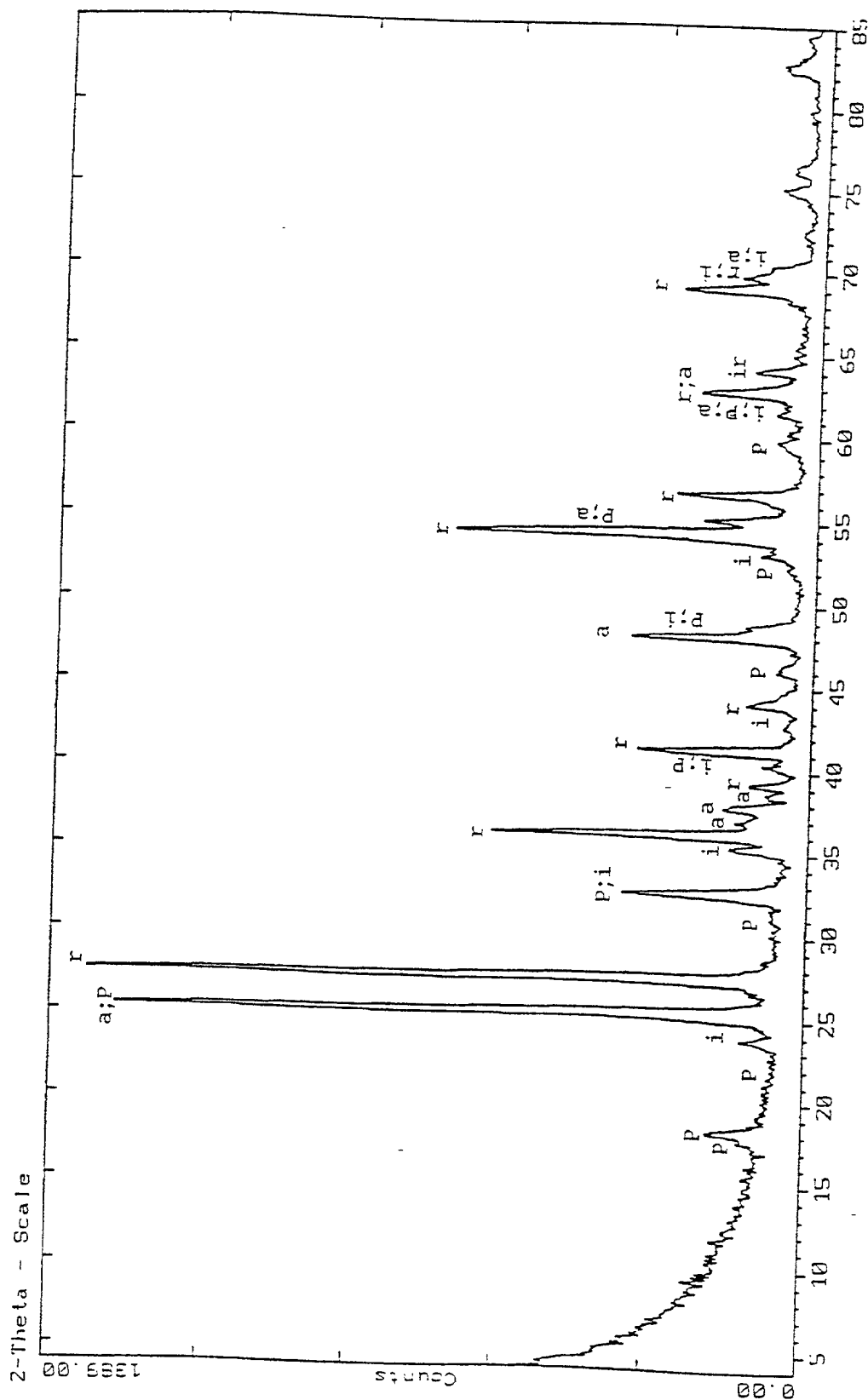


Figure 3

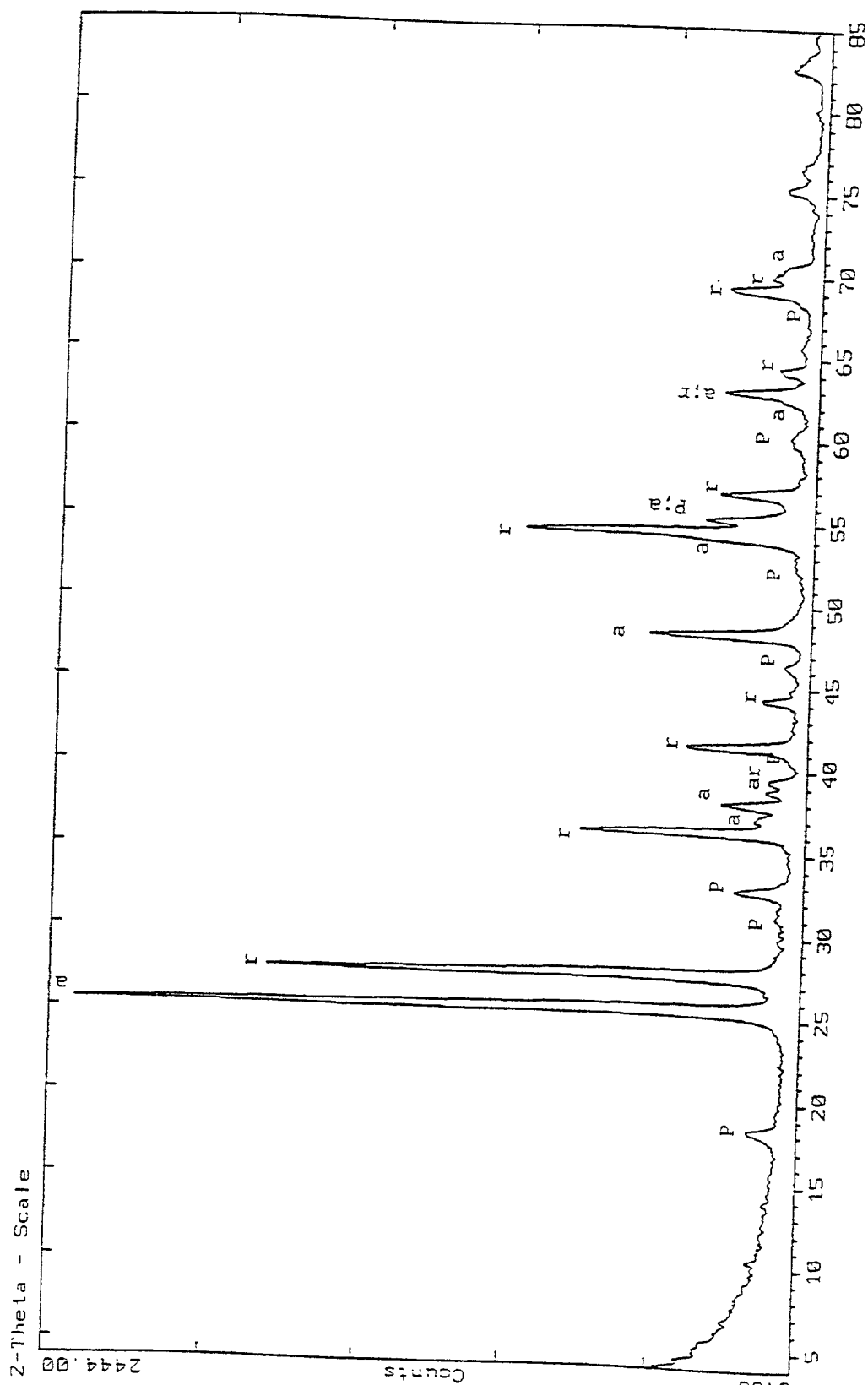


Figure 4

5/5

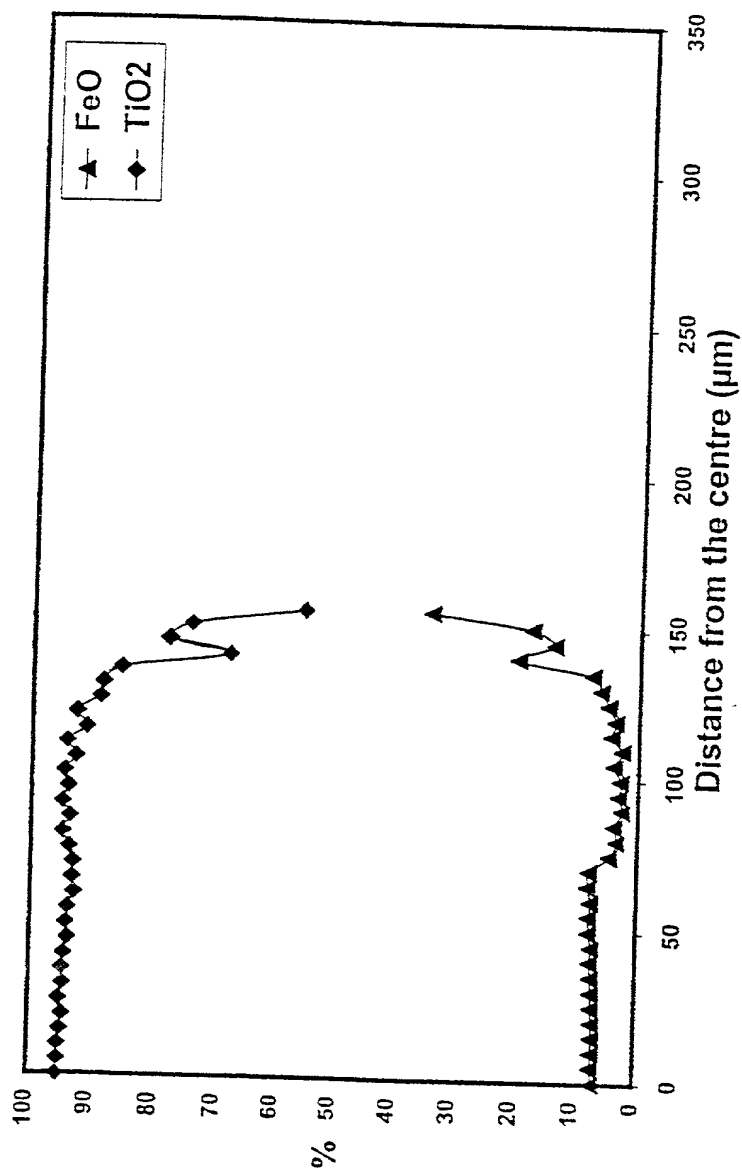


Figure 5

William E. Booth, Reg. No. 28,933
John F. Hayden, Reg. No. 37,640

Combined Declaration and Power of Attorney
Page 2 of 2 Pages

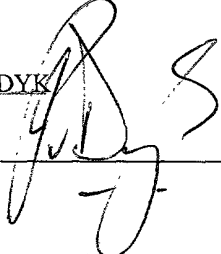
Address all telephone calls to TIMOTHY A. FRENCH at telephone number (617) 542-5070.

Address all correspondence to TIMOTHY A. FRENCH at:

FISH & RICHARDSON P.C.
225 Franklin Street
Boston, MA 02110-2804

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents issued thereon.

1-00
Full Name of Inventor: JACOBUS PHILIPPUS VAN DYK

Inventor's Signature: 


Date: 2001-5-2

Residence Address: 585 Gerhard Marais Street
Constantia Park
0010, Pretoria
REPUBLIC OF SOUTH AFRICA ZAX

Citizenship: South Africa

Post Office Address: 585 Gerhard Marais Street
Constantia Park
0010, Pretoria
REPUBLIC OF SOUTH AFRICA

2-00
Full Name of Inventor: NANNE MATTHEUS VEGTER

Inventor's Signature: 

Date: 2001-05-02

Residence Address: 796 Thomas Avenue
Arcadia 0083
Pretoria
REPUBLIC OF SOUTH AFRICA ZAX

Citizenship: South Africa

Post Office Address: 796 Thomas Avenue
Arcadia 0083
Pretoria
REPUBLIC OF SOUTH AFRICA

Combined Declaration and Power of Attorney

Page 3 of 3 Pages

3-00 Full Name of Inventor: CORNELIA PETRONELLA VISSER

Inventor's Signature: *CP Visser*

Date: 29 May 2001

Residence Address:

4 Daniel Road
Pierre van Ryneveld
Centurion, 0157
Pretoria *ZAX*
REPUBLIC OF SOUTH AFRICA

Citizenship:

South Africa

Post Office Address:

4 Daniel Road
Pierre van Ryneveld
Centurion, 0157
Pretoria
REPUBLIC OF SOUTH AFRICA

4-00 Full Name of Inventor: THOMAS DE LANGE

Inventor's Signature: *T de Lange*

Date: 8 May 2001

Residence Address:

18 Conglomerate Street
Zwartkop, Extension 8
Centurion, 0157
Pretoria *ZAX*
REPUBLIC OF SOUTH AFRICA

Citizenship:

South Africa

Post Office Address:

18 Conglomerate Street
Zwartkop, Extension 8
Centurion, 0157
Pretoria
REPUBLIC OF SOUTH AFRICA

5-00 Full Name of Inventor: JOHN DAVID WINTER

Inventor's Signature: *JD Winter*

Date: 8 Mar 2001

Residence Address:

3 Virgo Street
Elernore Vale, NSW 2287
AUSTRALIA *AUX*

Citizenship:

Australia

Post Office Address:

3 Virgo Street
Elernore Vale, NSW 2287
AUSTRALIA

Combined Declaration and Power of Attorney

Page 4 of 4 Pages

16-00 Full Name of Inventor: ERNEST ALAN WALPONE *Walpole*

Inventor's Signature: *[Signature]*

Date: 8 March 2001

Residence Address: 28 Chilcott Street
Lambton, NSW 2299 *AUX*
AUSTRALIA

Citizenship: Australia

Post Office Address: 28 Chilcott Street
Lambton, NSW 2299
AUSTRALIA

7-00 Full Name of Inventor: JOHANNES NELL *J. Nell*

Inventor's Signature: *[Signature]*

Date: 2001/06/04

Residence Address: 49 Duiker Avenue
Randpark Ridge, Extension 22
2156 Randburg
REPUBLIC OF SOUTH AFRICA *ZAX*

Citizenship: South Africa

Post Office Address: 49 Duiker Avenue
Randpark Ridge, Extension 22
2156 Randburg
REPUBLIC OF SOUTH AFRICA